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(54) Title: METHOD FOR OXIDISING A REACTANT GAS USING A CERAMIC ELECTROCHEMICAL REACTOR

(57) Abstract

A method of oxidizing a reactant gas is disclosed. The method uses an oxygen ion conducting ceramic honeycomb structure having a first set of channels and a second set of channels extending generally parallel to one another from a first face to a second face thereof, and wherein the second set of channels are sealed at the first and the second faces. The honeycomb structure further including a third set of channels which are transverse to and intersect the second set of channels, respectively. The method includes supplying the reactant gas to the first set of channels at the first face and supplying a gas containing free molecular oxygen to the third set of channels, thereby providing oxygen molecules in the second set of channels via the third set of channels. A chemical potential difference is applied between the first set of channels and the second set of channels, wherein the chemical potential difference causes the oxygen molecules to reduce to form oxygen ions, and wherein the ions diffuse through the ceramic honeycomb from the second set of channels to the first set of channels. The oxygen ions become oxygen molecules in the first set of channels which react with the reactant gas therein to form an oxidized reactant gas.

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METHOD FOR OXIDISING A REACTANT GAS USING A CERAMIC ELECTROCHEMICAL REACTOR

FIELD OF THE INVENTION

The present invention is generally related to electrochemical reactors, and more particularly is related to a method and system employing a ceramic honeycomb structure for adding or removing oxygen from a reactant gas stream.

BACKGROUND OF THE INVENTION

Oxygen tends to move from a gas containing a high concentration of oxygen to one of lower concentration. If the two gases are separated from each other by an oxygen ion conductor, oxygen will dissociate on one surface of the conductor and absorb electrons to form oxygen ions. These oxygen ions can then diffuse through the ionic conductor, leaving the entry surface with a deficiency of electrons. Emerging on the exit or low oxygen concentration side of the ion conductor, oxygen ions give up electrons to form molecular oxygen, leaving the exit surface with an excess of electrons. Thus, an electrical potential difference, or EMF, is set up between the two surfaces of the ion conductor. The greater the difference in oxygen content of the two gases, the greater will be the tendency of oxygen to diffuse through the conductor, and the greater will be the potential difference between the entry and exit surfaces.

These basic principles underlie the operation of oxygen sensing devices, which are generally well known in the art. Oxygen sensors function by monitoring the EMF developed across an oxygen ion conductor which is exposed to gases having different oxygen partial pressures. The reciprocal principle underlies the operation of oxygen separators (also called oxygen generators) such as disclosed in U.S. Patent No. 4,296,608. Voltage is applied to an oxygen ion conducting material and oxygen ions will be forced to flow across the material such that one gas will become richer in oxygen

than the other, resulting in a basic oxygen generator. A physical structure for an oxygen generator composed of an oxygen ion conducting material is disclosed in U.S. Patent No. 5,205,990.

It is always desirable to further improve upon such oxygen generators and form other systems and methods for a variety of uses.

SUMMARY OF THE INVENTION

The invention described herein uses a ceramic honeycomb structure prepared with either an oxygen ion conducting ceramic or a mixed electronic and oxygen ion conducting ceramic to either add or remove oxygen to or from a reactant gas stream to produce new chemical species or to purify an inert gas.

In the case of hydrocarbon gases, a gaseous material such as methane can be partially oxidized to form either methanol or diesel fuel which can be subsequently condensed to liquid form. Converting a gaseous hydrocarbon to a liquid hydrocarbon is advantageous in the transport of fuels from remote sites, such as the Alaskan North Slope oilfields, where the transport of gaseous hydrocarbons is economically unfeasible.

In the case of inert gas purification, oxygen impurities can be removed from inert gas streams using this invention in a more economic fashion than the current method that utilizes platinum catalyst beds and hydrogen to remove oxygen. The present invention will provide a dry reduced oxygen inert gas stream instead of the "wet" reduced oxygen inert gas stream provided by prior art technology.

The invention is based on a ceramic honeycomb fabricated with an oxygen ion conducting ceramic such as yttria stabilized bismuth oxide or yttria stabilized zirconium oxide. The ceramic honeycomb can also be fabricated using a mixed conducting ceramic (a ceramic with both electronic and oxygen ion conductivity) such as strontium iron cobalt oxide or lanthanum strontium cobalt oxide. In the case of a ceramic honeycomb fabricated with an oxygen

ion conducting ceramic, an oxide electrode material such as lanthanum lead manganite or lanthanum strontium manganite is applied to the honeycomb channel surfaces to facilitate the conversion of oxygen gas to oxygen ions and vice versa. In addition, a silver metallization is applied over the oxide electrode to facilitate the distribution of current over the oxide electrode surface. Wires are bonded to the inside of parallel honeycomb channel rows, for example, to provide for the application or flow of current.

In the case of a ceramic honeycomb fabricated with a mixed conducting ceramic material, no oxide electrode, metallization, or wiring is required for operation. For some applications a precious metal or base metal catalyst can be applied to the channel surfaces to facilitate the formation of certain organic compounds when the reactant gas reacts with the oxygen being provided at the surface of the honeycomb channels.

In order to fabricate an electrochemical reactor the ceramic honeycomb is "manifolded" to separate the air stream from the reactant stream. Similarly, in order to fabricate an inert gas purification device, manifolding is required to separate the inert gas stream from the extracted oxygen stream.

In an electrochemical reactor, an inlet plenum is coupled to the ceramic honeycomb and includes a reactant gas inlet port which directs the input reactant gas into a first set of channels in the honeycomb. The reactor also includes an outlet plenum which is coupled to the honeycomb and includes a product gas outlet port which directs the product gas away from the first set of channels in the honeycomb. The reactor also includes an oxygen containing process gas inlet manifold and a waste process gas outlet manifold. The inlet manifold delivers an oxygen containing gas to a set of sealed second channels in the honeycomb and the outlet manifold serves to remove an oxygen depleted process gas from the sealed second channels. The oxygen containing process gas enters the sealed second channels via

the inlet manifold and oxygen ions conduct through the honeycomb structure to the first channels. The oxygen ions form molecular oxygen in the first channels and react with the reactant gas provided via the inlet plenum to thereby produce the product gas which is removed via the outlet plenum.

In an inert gas purification device, the ceramic honeycomb structure also includes an inlet plenum and an outlet plenum. The inlet plenum delivers an oxygen containing inert gas to the second channels of the purification device and the outlet plenum directs a purified inert gas from the second channels away therefrom. The purification device further includes an oxygen outlet manifold which removes oxygen from a set of sealed first channels, wherein the oxygen was removed from the inert gas, thus purifying the inert gas.

According to another aspect of the present invention, a variable purity inert gas purification device is disclosed which provides for varying levels of inert gas purity based on passing the inert gas through the honeycomb multiple times. For example, the purity of an inert gas is increased without compromising the physical integrity of the honeycomb body by separating the honeycomb into two zones and passing the inert gas through the first zone in a first direction and the second zone in an opposite direction, thereby effectuating a multi-pass inert gas purification device. Varying levels of inert gas purity is also provided based on a controllable manifold scheme. For example, for a first low purity level, the oxygen containing inert gas passes through the honeycomb structure a single time. For higher inert gas purity levels, the inert gas is directed through the honeycomb structure a plurality of times using controllable baffles in conjunctions with the manifolds.

To the accomplishment of the foregoing and related ends, the invention comprises the features hereinafter fully described and particularly pointed out in the claims. The following description and the annexed drawings set forth in detail certain illustrative embodiments of the invention.

These embodiments are indicative, however, of but a few of the various ways in which the principles of the invention may be employed. Other objects, advantages and novel features of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a perspective view of an oxygen generating apparatus employing a ceramic honeycomb structure;

Figure 2 is a perspective view of an apparatus employing a honeycomb structure used as an electrochemical reactor according to the present invention;

Figure 3 is a perspective view of the electrochemical reactor of Figure 2 employing a manifolding system according to the present invention;

Figure 4 is a schematic diagram of electrochemical reactions using a mixed conduction ceramic according to the present invention;

Figure 5 is a perspective view of an apparatus employing a honeycomb structure used as an inert gas purification device according to the present invention;

Figure 6 is a perspective view of the inert gas purification device of Figure 4 employing a manifolding system according to the present invention;

Figure 7 is a schematic diagram of an inert gas purification process using an oxygen ion conducting ceramic according to the present invention;

Figure 7a is a side view of an inert gas purification device employing a honeycomb structure having an alternative wiring scheme according to the present invention;

Figure 8 is a schematic diagram illustrating a manifolding scheme for a multi-pass inert gas purification device according to the present invention;

Figure 9 is a schematic diagram illustrating a cross section of the manifolding scheme of Figure 8 according to the present invention;

Figure 10 is a schematic diagram illustrating another manifolding scheme for a multi-pass inert gas purification system according to the present invention; and

Figure 11 is a schematic diagram illustrating still another manifolding scheme for a multi-pass inert gas purification system according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be described with reference to the drawings wherein like reference numerals are used to refer to like elements throughout. The present invention relates to a ceramic honeycomb structure composed of either an oxygen ion conducting ceramic or a mixed electronic and oxygen ion conducting ceramic to either add or remove oxygen to or from a reactant gas stream to produce new chemical species or to purify an inert gas.

In Figure 1 a ceramic honeycomb body 12 is illustrated. The ceramic honeycomb body 12 is made of an oxygen ion conducting material or a mixed electrically conducting and oxygen ion conducting material (hereinafter referred to as a "mixed conducting material"), as may be desired. Exemplary materials include yttria stabilized bismuth oxide, yttria stabilized zirconium oxide, strontium iron cobalt oxide or lanthanum strontium oxide, however, other materials may be used and are contemplated as falling within the scope of the present invention. The honeycomb body 12 includes a first plurality or set of channels 14 and a second plurality or set of channels 16 extending therethrough from a front face 18 to a back face 20. Preferably, the channels 14 and 16 are arranged in alternating rows, resembling a striped pattern laterally across the faces 18 and 20 of the ceramic honeycomb body 12. In Figure 1, the second set of channels 16 are illustrated as sealed at the front and back faces 18 and 20, however, as will be described in greater detail *infra*, depending on the application, either the first set of channels 14 or the

second set of channels 16 may be sealed and such sealing may be accomplished, for example, using a glass sealing material or a ceramic cement.

The system of Figure 1 further includes a voltage source 22 electrically connected to the channels 14 and 16 through electrode connectors 24 and 26 located on a top portion 28 of the honeycomb body 12, respectively. A connection methodology is implemented such that each of the first channels 14 are electrically connected in parallel and each of the second channels 16 are also electrically connected in parallel. The voltage source 22 is operable to apply a voltage across the electrodes 24 and 26 such that a voltage potential is created across the first and second channels 14 and 16, thereby enabling oxygen ion conduction through the ceramic honeycomb body 12 from one channel to another.

The honeycomb body 12 further includes side faces 36 and 37 which may be used to access the first or second set of channels 14, 16, respectively. Typically, a side face such as the face 36 is used to access the sealed set of channels, such as the second set of channels 16 illustrated in Figure 1. Such access is achieved by drilling one or more holes 38 in the side face 36 in locations corresponding to the sealed channels. An exemplary honeycomb structure for performing the above invention is disclosed in U.S. Patent 5,205,990 and U.S. Patent Application Serial Nos. 08/926,366 and 08/986,161, respectively, which are hereby incorporated by reference in their entirety.

According to one exemplary embodiment of the present invention, an electrochemical reactor for use in adding oxygen to a reactant gas stream to produce a new chemical species is disclosed in Figures 2 and 3 at reference numeral 40. In Figure 2, the electrochemical reactor 40 employs the honeycomb structure 12 of Figure 1. In Figure 2 the honeycomb 12 is rotated clockwise by 90 degrees for purposes of clarity, however, any honeycomb

orientation may be utilized in the present invention. As in Figure 1, the first set of channels 16 extend through the honeycomb 12 from the first or front face 18 to the second or back face 20, while the second set of channels are sealed at the first and second faces 18 and 20, respectively. According to exemplary embodiments of the present invention, the channels 16 are sealed with a glass sealing material, a ceramic cement, or ceramic plugs, however, other materials may be utilized and are contemplated as falling within the scope of the present invention. The holes 38 preferably correspond to each of the sealed second channels 16, are formed in the side or third face 36 and allow access to the second channels 16 for supplying an oxygen containing process gas such as air to the reactor 40.

Figure 3 illustrates the reactor 40 of Figure 2 employing a manifolding scheme according to an exemplary embodiment of the present invention. The reactor 40 has an inlet plenum 42 which is bonded or otherwise coupled to the first face 18 of the honeycomb body 12 with, for example, a sealing glass or ceramic cement. The inlet plenum preferably is fabricated from a high temperature alloy such as Inconel, however, other materials may be utilized and any suitable material is contemplated as falling within the scope of the present invention. The inlet plenum 42 has a reactant gas input port 44 which couples to a reactant gas source such as methane and directs the reactant gas into the first channels 14 at the first face 18 of the honeycomb 12. In the above preferred manner, a reactant gas is introduced into the reactor 40 without the introduction of impurities or the loss of reactant gas.

The reactor 40 further includes an outlet plenum 46 which is bonded or otherwise coupled to the second face of the honeycomb body 12 with, for example, a sealing glass or ceramic cement. The outlet plenum has a product gas output port 48 which couples to a product gas reservoir, container, gas line, etc. The output port 48 thus directs the product gas from the second channels 16 of the honeycomb 12 at the second face 20 via the

outlet plenum 46. The outlet plenum 46 thus directs the product gas away from the reactor 40 to a suitable storage or transfer apparatus while preventing contamination of the product gas.

The operation of the electrochemical reactor 40 according to a preferred embodiment of the present invention proceeds in the following manner. Air or another oxygen containing process gas is flowed through the sealed second channels 16 of the reactor (the second channels 16 may alternatively be referred to as cathode channels) via the inlet manifold 50. The reactant gas is passed through the first (open) channels 14 (the first channels 14 may alternatively be referred to as anode channels) of the ceramic honeycomb 12 via the plenums 42 and 46. The reactant gas will have an oxygen partial pressure much less than 10^{-20} atmospheres while the process gas has an oxygen partial pressure of around 0.21 atmospheres (for air). This partial pressure difference sets up a large chemical potential difference between the anode and cathode channels resulting in an electrochemical potential.

The electrochemical potential is the driving force for the diffusion of oxygen from the cathode channels through the ceramic to the anode channels. Since the ceramic material 12 is impervious to gaseous flow, the diffusion of gaseous oxygen cannot occur. However, since the ceramic can conduct oxygen ions, the oxygen atoms on the cathode side can be reduced to O^{-2} ions, diffuse through the ceramic material, and be "oxidized" on the anode side to form gaseous oxygen. In order to accomplish this, electrons are provided to the oxygen atoms on the cathode side and removed from them on the anode side. Electron flow can be accomplished by either internally or externally shorting the cathode and anode channels (*i.e.*, the first and second channels 14 and 16).

Internal shorting can be accomplished by using a mixed conducting ceramic that conducts both electrons and oxygen ions. In this way, oxygen

ions are flowing from the cathode to the anode while electrons are flowing in the opposite direction. This is the preferred way of accomplishing this process since it does not involve the use of wires (external shorting) that add cost and complexity to the reactor 40. Alternatively, however, an oxygen ion conductor that has no electronic conductivity may be used if the surfaces of the ceramic are coated with an oxide electrode and metallization as well as being wired in such a way as to short the anode channels to the cathode channels. Oxygen may also be "pumped" from the anode to the cathode side by applying a current to a wired ceramic honeycomb, but this is not preferred as it adds operating cost by the use of electric power.

In operation, a reactant gas such as methane or another hydrocarbon gas is supplied to the anode or first channels 14 of the ceramic honeycomb 12 through the inlet plenum 42. Air or another gas containing free molecular oxygen is supplied to the sealed cathode or second channels 16 of the ceramic honeycomb 12 via the process gas manifold 50. The oxygen molecules (O_2) in the cathode or second channels 16 are reduced on the ceramic channel surface to form oxygen ions (O^{-2}). These ions diffuse through the mixed conducting ceramic 12 to the anode side (first channels 14) under the influence of the chemical potential difference between the oxygen containing gas in the cathode channels and the reactant gas in the anode channels. On the surface of the ceramic in the anode channels (the first channels 14), the oxygen ions are "oxidized" to become oxygen gas molecules that are available to react with the reactant gas to form chemical products. An exemplary reaction diagram is illustrated schematically in Figure 4. The reaction products then exit through the outlet plenum 46 of the reactor 40. The oxygen depleted process gas in the cathode channels is removed via the cathode outlet manifold 52.

The electrochemical reactor 40 may further include a catalyst coating within the first channels (the anode channels) in order to facilitate the reaction

of the oxygen with the reactant gas therein. The catalyst coating may be, for example, a precious metal or base metal catalyst such as platinum, palladium, nickel or chrome, however, any material which catalyzes the reaction of the oxygen and the appropriate reactant gas may be utilized and is contemplated as falling within the scope of the present invention. Preferably, however, the catalyst coating material is selected based on the particular type of reactant gas and the type of chemical reaction desired.

According to an alternative embodiment of the present invention, an inert gas purification device may also be fabricated in a similar fashion. In such a case, however, the sealed channels are the anode or first channels 14 and the open channels are the cathode or second channels 16. To use the device described above for inert gas purification the inert gas containing oxygen would have to be pressurized to a high pressure. A high pressure is required to create the partial pressure difference necessary to provide the electrochemical potential for oxygen diffusion from the inert gas on the cathode side to the anode side where oxygen is concentrated. For instance, to purify an inert gas to a 0.1% oxygen concentration level, the pressure difference would have to be 210 times. For a gas having a 0.01% oxygen concentration level, the pressure difference would have to be 2100 times thus much higher for higher purity. Such pressures are not preferred for the ceramic honeycomb device, yet are still contemplated as falling within the scope of the present invention.

The required chemical potential, however, can be achieved by applying an electrical potential across the electrolyte by flowing current across the ceramic electrolyte 12. In this way oxygen is "pumped" from the cathode side to the anode side. For inert gas purification, an oxygen ion conducting ceramic is used to fabricate the ceramic honeycomb 12. An exemplary purification device is illustrated in Figure 5 at reference numeral 100. As discussed *supra*, in an inert gas purification application, the first channels 14

(the anode channels) are sealed, for example, with a glass sealing material or ceramic cement, and the second channels 16 (the cathode channels) are open and extend through the honeycomb 12 from the first or front face 18 to the second or back face 20.

An oxide electrode material and metallization is applied to the channel surfaces of the ceramic honeycomb 12. For example, an oxide electrode material may include lanthanum lead manganite or lanthanum strontium manganite, however, other suitable materials may be utilized and are contemplated as falling within the scope of the present invention. In addition, the metallization may include silver or other highly electrically conductive materials. Wires 102 and 104 are applied across the anode and cathode channels at either the first or second faces 18 and 20 (or both). Current is applied across the channels walls of the honeycomb 12 separating the anode and cathode channels 14 and 16 in such a way that oxygen is transported from the open cathode or second channels 16 through the oxygen ion conducting ceramic 12 to the sealed anode or first channels 14.

An exemplary manifolding scheme according to one embodiment of the present invention is illustrated in Figure 6. The inert gas purification device 100 includes an inlet plenum 110 bonded or otherwise coupled to the first face 18 of the honeycomb 12. The inlet plenum 110 includes an inert gas inlet port 112 which operates to deliver an oxygen containing inert gas requiring purification from a source location to the device 100. The inlet plenum 110 thus serves to direct the gas requiring purification to the open second channels 16 at the first face 18 of the honeycomb.

The purification device 100 also includes an outlet plenum 114 which is bonded or otherwise coupled to the second face 20 of the honeycomb 12. The outlet plenum 114 includes a purified inert gas outlet port 116 which operates to couple to a storage or gas transfer apparatus (not shown). The outlet plenum 114 thus operates to collect the purified inert gas (having some

oxygen removed) from the open second channels 16 at the second face 20 of the honeycomb 12.

The purification device 100 further includes an oxygen outlet manifold 118 which is coupled to either the third or fourth faces 36 or 37 of the honeycomb 12. The oxygen outlet manifold 118 is coupled to the holes 36 of Figure 5 which connect to the sealed first channels 14 and operates to draw out the oxygen which diffuses through the channel walls. Therefore at least a portion of the oxygen which exits the device 100 via the oxygen outlet manifold 118 is the oxygen which was removed from the input inert gas.

In operation, the oxygen containing inert gas (*e.g.*, nitrogen) is supplied to the open cathode or second channels 16 through the inlet plenum 110. Oxygen molecules in the gas are reduced to oxygen ions at the oxide electrode/oxygen ion conducting ceramic interface on the cathode or second channel surfaces. Under the influence of the applied electrical potential, the oxygen ions are conducted through the oxygen ion conducting ceramic 12 to the anode or first channel surface. At the oxide electrode/oxygen ion conducting ceramic interface on the anode channel surfaces, the oxygen ions are "oxidized" to form oxygen gas molecules. An exemplary reaction diagram is illustrated schematically in Figure 7. The purified inert gas exits the ceramic honeycomb device through the outlet plenum 114 and the removed oxygen exits the oxide electrode/oxygen ion conducting ceramic interface through the oxygen outlet manifold 118.

In Figure 5, the wiring of the first and second channels 14 and 16 is illustrated at the first face 18 of the honeycomb structure 12. As illustrated in Figure 6, the inlet plenum 110 is coupled to the first face 18 and care is preferably taken to avoid interaction between the inlet plenum 110 and the electrical current supplied to the device via the wires 102 and 104. In order to further improve the device 100 of the present invention, an alternative wiring scheme is illustrated in Figure 7a.

To avoid interaction between the inlet plenum 110 or the outlet plenum 114 with the current carried by the wires 102 and 104, holes 119a are drilled or otherwise formed through the honeycomb structure 12 from one of the side faces 36, 37 at some distance 119b away from an end face 18, 20 of the honeycomb structure 12 to access the channels 14 and 16 of the device 100. Wires (not shown) or other type of conductive members or materials are then inserted through the holes 119a and electrical contact is established with the electrode material within the channels 14 and 16. A sealing material such as a glass sealing material or a ceramic cement is then preferably placed around the wires to provide a gas tight seal around the wires to thereby prevent leakage and/or contamination of the purified gas. According to the above alternative embodiment of the present invention, the wiring scheme of Figure 7a prevents an accidental electrical contact between one of the plenums 110, 114 and the wiring, thus eliminating the risk of shorting out the device 100 and causing damage to the wires and/or the plenums 110, 114.

The purity level of the inert gas which exits the purification device is a function of the size of the honeycomb structure. Therefore if the length of the various channels within the oxygen ion conducting ceramic honeycomb structure are increased, the purity level of the exit gas is improved. That is, the exit gas contains less oxygen than would otherwise exist. Therefore the desired purity performance of the purification device (oxygen scrubber) may be customized by varying the channel lengths of the honeycomb structure.

Although increasing the length of the honeycomb structure is one method of increasing the purity level of the inert gas, increasing the length of the honeycomb may weaken the structural integrity of the honeycomb and may result in an increased potential of physical damage to the structure due to external stresses. Therefore one alternative method of improving the purity level of the inert gas is to cascade multiple honeycombs in series. In this manner, each honeycomb structure maintains its structural integrity and the

purity level may be customized by adding to or removing the number of honeycomb structures in the cascaded arrangement.

In another alternative arrangement, the purity level of the inert gas may be improved using a novel manifolding scheme. Figures 8 and 9 illustrate a manifolding scheme to increase the purity level of the inert gas without compromising the physical integrity of the honeycomb structure according to an exemplary embodiment of the present invention. In Figures 8 and 9, which are side views of a purification device 200, the first face 18 of the honeycomb structure 12 is covered by a first face manifold 202 which separates the first face 18 of the honeycomb 12 into two sets of open channels 204a and 204b, wherein the two sets of open channels 204a and 204b are isolated from one another by a separator 206 such as a baffle. One set of open channels 204a is dedicated to receiving the inlet gas 208 for purification via a raw gas inlet 210 while the second set of open channels 204b is dedicated to removing the purified gas from the device 200 via a purified gas outlet 212.

A manifold plenum or second face manifold 214 is coupled to a second face 20 of the honeycomb 12 and operates to direct the gas undergoing purification from the first set of open channels 204a into the second set of open channels 204b to thereby increase the effective channel length experienced by the purified gas by 2X. According to Figures 8 and 9, for a given honeycomb structure 12, the above manifolding scheme provides a substantial increase in the inert gas purity, but correspondingly reduces the amount of purified gas generated per unit time since the number of dedicated inlet and outlet channels is reduced.

The manifolding scheme of Figures 8 and 9 may be further expanded to redirect the gas being purified back through the honeycomb multiple times by using multiple baffles and manifolds to separate the channels into a plurality of individual sets. For example, the device 200 may provide for a

plurality of differing inert gas purity levels by selectively controlling a plurality of baffles in the first face manifold 202 and the second face manifold 214, respectively. By opening and closing various combinations of baffles within the manifolds 202 and 214, the number of times in which the inert gas is passed through the open channels is controlled, wherein the number of passes is related to the desired inert gas purity levels.

Another alternative manifolding scheme is illustrated in Figure 10. In Figure 9, the oxygen scrubber (the ceramic honeycomb structure) employs a feedback or recirculation manifold which allows the channels in the structure to be utilized multiple times in purifying a single volume of gas. That is, the purified gas which exits the second face of the honeycomb is fed back to the first face of the structure to again pass through the channels. The feedback or recirculation may be achieved through a series of baffles on the inlet, the outlet and the recirculation path, respectively. Each of the baffles is preferably controlled by a controller (not shown) which opens and closes the baffles at predetermined times according to, for example, programmed instructions.

The multi-pass inert gas purification system 300 is similar in many respects to the system 100 of Figure 6. System 300, however, further includes a recirculation path 302 which couples the outlet port 116 back to the inlet port 112 via a recirculation baffle 304 or other type controllable valve mechanism. In addition, an outlet baffle 306 or valve is provided in the outlet gas flow path and an inlet baffle 308 or valve is provided in the inlet gas flow path, respectively. The baffles 304, 306 and 308 may be operated in conjunction with one another either manually or via a controller to selectively recirculate a purified inert gas through the honeycomb structure 12 multiple times.

An exemplary mode of operation is as follows. To input a volume of source gas into the structure, the inlet baffle 308 and the recirculation baffle

304 are opened and the outlet baffle 306 is closed. After a predetermined time (corresponding to filling the volume of the honeycomb structure 12) the inlet baffle 308 is closed and the recirculation baffle 304 is kept open. The purified gas then is fed back and recirculates through the honeycomb structure 12 via the recirculation path 302 a number of times, each time becoming more pure via the continued scrubbing of oxygen from the inert gas. After a predetermined time (corresponding to the desired purity level) the recirculation baffle 304 is closed and the outlet baffle 306 is opened to remove the purified inert gas. As illustrated in the manifolding scheme of Figure 10, the volume of gas generated is not reduced using the recirculation system since each of the open channels may be used for scrubbing instead of having sets of channels dedicated for specified circulation paths.

The recirculation path 302 may be maintained, if necessary, by a draft inducer system to keep the gas circulating. Preferably, such a draft inducement system incorporates a filter to ensure that the purified gas is not contaminated. The draft inducement may be a physical apparatus or it may differ as illustrated in Figure 11.

As illustrated in Figure 11, an exemplary feedback or recirculation system 320 incorporates a cooling device 322 such as a thermoelectric chiller or any form of cooling means to cool the gas in the recirculation path 302 when the recirculation baffle 304 is open. The cooled gas in the recirculation path 302 contracts and occupies less volume, thereby drawing a vacuum in the recirculation path 304. A check valve 324 in the recirculation path 302 near the gas inlet port 112 prevents gas from traveling backwards from the inlet through the recirculation path 302, thereby making the recirculation path 302 unidirectional. The vacuum generated by the cooled gas then pulls the gas being purified in the scrubber 12 through the device, thereby providing a draft inducing mechanism in the system 320. In addition, as may be desired, a heating unit (not shown) may be utilized in the recirculation path 302 near

the gas inlet port 102 to heat up the purified gas after it passes the check valve 324 to maintain a high efficiency. Other flow mechanisms may alternatively be used and each is contemplated as falling within the scope of the present invention.

Although the invention has been shown and described with respect to a certain preferred embodiment or embodiments, it is obvious that equivalent alterations and modifications will occur to others skilled in the art upon the reading and understanding of this specification and the annexed drawings. In particular regard to the various functions performed by the above described components (assemblies, devices, circuits, etc.), the terms (including a reference to a "means") used to describe such components are intended to correspond, unless otherwise indicated, to any component which performs the specified function of the described component (*i.e.*, that is functionally equivalent), even though not structurally equivalent to the disclosed structure which performs the function in the herein illustrated exemplary embodiments of the invention. In addition, while a particular feature of the invention may have been disclosed with respect to only one of several embodiments, such feature may be combined with one or more other features of the other embodiments as may be desired and advantageous for any given or particular application.

What is claimed is:

1. A method of oxidizing a reactant gas using an oxygen ion conducting ceramic honeycomb structure having a first set of channels and a second set of channels extending generally parallel to one another from a first face to a second face thereof, and wherein the second set of channels are sealed at the first and second faces, the honeycomb structure further including a third set of channels which are transverse to and intersect the second set of channels, respectively, comprising the steps of:

supplying the reactant gas to the first set of channels at the first face;

supplying a gas containing free molecular oxygen to the third set of channels, thereby providing oxygen molecules in the second set of channels via the third set of channels; and

applying a chemical potential difference between the first set of channels and the second set of channels, wherein the chemical potential difference causes the oxygen molecules to reduce to form oxygen ions, and wherein the ions diffuse through the ceramic honeycomb from the second set of channels to the first set of channels, and wherein the oxygen ions become oxygen molecules in the first set of channels which react with the reactant gas therein to form an oxidized reactant gas.

2. The method of claim 1, further comprising the step of collecting the oxidized reactant gas from the first set of channels at the second face of the honeycomb structure.

3. The method of claim 2, wherein the step of collecting the oxidized reactant gas from the first set of channels at the second face of the honeycomb structure comprises:

coupling an outlet plenum having a product gas outlet port to the second face of the honeycomb structure;

coupling a product gas storage apparatus to the product gas outlet port; and

delivering the oxidized reactant gas from the first set of channels at the second face of the honeycomb structure to the product gas storage apparatus via the outlet plenum.

4. The method of claim 1, wherein the reactant gas comprises a hydrocarbon gas.

5. The method of claim 4, wherein the hydrocarbon gas comprises methane.

6. The method of claim 1, wherein the step of supplying the reactant gas to the first set of channels at the first face of the honeycomb structure comprises:

coupling an inlet plenum having a reactant gas input port to the first face of the honeycomb structure;

coupling a reactant gas source to the reactant gas input port; and

delivering the reactant gas to the first set of channels at the first face of the honeycomb structure via the inlet plenum.

7. The method of claim 6, further comprising the step of sealing the inlet plenum with a glass sealing material or a ceramic cement to the first face of the honeycomb structure to thereby prevent leakage or contamination of the reactant gas at the first face.

8. The method of claim 1, further comprising the step of catalyzing the reaction of the reactant gas and the oxygen molecules in the first set of channels.

9. The method of claim 8, wherein the step of catalyzing the reaction of the reactant gas and the oxygen molecules comprises forming a catalyst film in the first set of channels, wherein the catalyst film comprises a precious metal or a base metal catalyst.

10. The method of claim 1, wherein applying a chemical potential difference between the first and second set of channels comprises supplying the reactant gas with an oxygen partial pressure which is substantially less than an oxygen partial pressure of the gas containing free molecular oxygen.

11. A ceramic based electrochemical reactor, comprising:

an oxygen ion conducting ceramic structure having one or more first channels and one or more second channels extending therethrough from a first face to a second face thereof, wherein the first channels and the second channels are generally parallel to one another and wherein the second channels are sealed at the first and second faces, and wherein the ceramic structure further comprises one or more third channels extending transverse to and intersecting the one or more second channels, respectively, and extending through the ceramic structure between a third face and a fourth face thereof;

an inlet plenum coupled to the first face of the ceramic structure, the inlet plenum including a reactant gas input port for providing a reactant gas to the reactor, wherein the inlet plenum directs the reactant gas into the first channels at the first face;

an outlet plenum coupled to the second face of the ceramic structure, the outlet plenum including a product gas output port for directing a product gas away from the reactor, wherein the outlet plenum collects the product gas from the first channels at the second face into the outlet port; and

an oxygen containing process gas inlet manifold coupled to the third face of the ceramic structure, wherein the inlet manifold is operable to deliver a process gas containing free molecular oxygen into the sealed second channels via the third channels at the third face.

12. The electrochemical reactor of claim 11, further comprising a waste process gas outlet manifold coupled to the third channels on the fourth face of the ceramic structure, wherein the outlet manifold is operable to remove an oxygen depleted process gas from the sealed second channels via the third channels at the fourth face.

13. The electrochemical reactor of claim 11, wherein the oxygen ion conducting ceramic structure is a mixed oxygen ion conducting and electronic conducting material which is operable to conduct both electrons and oxygen ions therethrough.

14. The electrochemical reactor of claim 13, wherein the mixed oxygen ion conducting and electronic conducting material is selected from the group consisting of strontium iron cobalt oxide and lanthanum strontium cobalt oxide.

15. The electrochemical reactor of claim 11, further comprising a catalyst film formed in the one or more first channels, wherein the catalyst film facilitates the formation of reactant gas compounds in the one or more first channels.

16. The electrochemical reactor of claim 15, wherein the catalyst film comprises a precious metal or base metal catalyst.

17. The electrochemical reactor of claim 16, wherein the precious metal or base metal catalyst comprises platinum, palladium, nickel or chrome.

18. The electrochemical reactor of claim 11, wherein the inlet plenum and the outlet plenum are coupled to the ceramic structure with a sealing glass or a ceramic cement to thereby prevent leakage or contamination of the input reactant gas and the output product gas and ensure a secure connection across a range of temperatures.

19. An inert gas purification device, comprising:

an oxygen ion conducting ceramic structure having one or more first channels and one or more second channels extending therethrough from a first face to a second face thereof, wherein the first channels and the second channels are generally parallel to one another and wherein the first channels are sealed at the first and second faces, and further wherein the first and second channels are lined with an electrode film;

one or more third channels extending transverse to and intersecting the one or more first channels, respectively, and extending through the ceramic structure from a third face;

a power supply coupled to the electrode layers of the first and second channels, respectively, wherein the power supply is operable to provide an electrical potential across portions of the ceramic between the first and second channels;

an inlet plenum coupled to the first face of the ceramic structure, the inlet plenum including an inert gas inlet port for providing an oxygen

containing inert gas to the purification device, wherein the inlet plenum directs the oxygen containing inert gas into the second channels at the first face; and

an outlet plenum coupled to the second face of the ceramic structure, the outlet plenum including a purified inert gas outlet port for directing a purified inert gas away from the purification device, wherein the outlet plenum collects the purified inert gas from the second channels at the second face into the outlet port.

20. The inert gas purification device of claim 19, further comprising an oxygen outlet manifold coupled to the third channels at the third face of the ceramic structure, wherein the oxygen outlet manifold is operable to remove oxygen from the sealed first channels via the third channels at the third face.

21. The inert gas purification device of claim 19, further comprising:

a plurality of fourth channels extending transverse to and intersecting the one or more first channels and the one or more second channels; and

a conductive wire within each of the plurality of fourth channels, wherein the conductive wires make electrical contact with the one or more first channels and the one or more second channels such that the one or more first channels are electrically connected in parallel along a given fourth channel and the one or more second channels are electrically connected in parallel along another given fourth channel,

wherein the conductive wires are coupled to the power supply and are operable to deliver the electrical potential between the first and second channels.

22. The inert gas purification system of claim 19, further comprising a recirculation system coupled between the outlet plenum and the inlet plenum, wherein the recirculation system is operable to direct a purified inert

gas back through the honeycomb structure, thereby providing for additional purification of the purified inert gas.

23. The inert gas purification device of claim 22, wherein the recirculation system comprises:

an outlet baffle in the purified inert gas outlet port;

an inlet baffle in the inert gas inlet port; and

a recirculation path between purified inert gas outlet port and the inert gas inlet port, wherein when the outlet baffle and the inlet baffle are closed, the purified inert gas recirculates through the honeycomb structure through the recirculation path until the outlet baffle is opened.

24. The inert gas purification device of claim 23, further comprising a recirculation baffle in the recirculation path, wherein when the recirculation baffle is closed, purified inert gas is prevented from recirculating through the honeycomb structure.

25. The inert gas purification device of claim 23, further comprising a draft inducer in the recirculation path.

26. The inert gas purification device of claim 25, wherein the draft inducer comprises a cooling device for cooling the purified inert gas in the recirculation path, wherein the cooled purified inert gas occupies less volume in the recirculation path, thereby drawing a vacuum therein and facilitating recirculation of gas through the recirculation path.

27. A multi-pass inert gas purification device, comprising:

an oxygen ion conducting ceramic structure having one or more first channels and one or more second channels extending therethrough from a

first face to a second face thereof, wherein the first channels and the second channels are generally parallel to one another and wherein the first channels are sealed at the first and second faces, and further wherein the first and second channels are lined with an electrode film;

one or more third channels extending transverse to and intersecting the one or more first channels, respectively, and extending through the ceramic structure from a third face;

a power supply coupled to the electrode layers of the first and second channels, respectively, wherein the power supply is operable to provide an electrical potential across portions of the ceramic between the first and second channels;

a first face manifold coupled to the first face of the ceramic structure, wherein the first face manifold includes a baffle therein for separating the first face manifold into two zones, wherein a first zone receives an oxygen containing inert gas and directs the inert gas into a first subset of the second channels at the first face corresponding to the first zone, and wherein a second zone of the first face manifold receives a purified inert gas from a second subset of the second channels at the first face corresponding to the second zone;

a second face manifold coupled to the second face of the ceramic structure, wherein the second face manifold receives a purified inert gas from the first subset of second channels corresponding to the first zone and directs the purified inert gas into the second subset of second channels corresponding to the second zone,

wherein the first face manifold and the second face manifold provide for the direction of the oxygen containing inert gas through more than one of the second channels, thus improving an inert gas purification level.

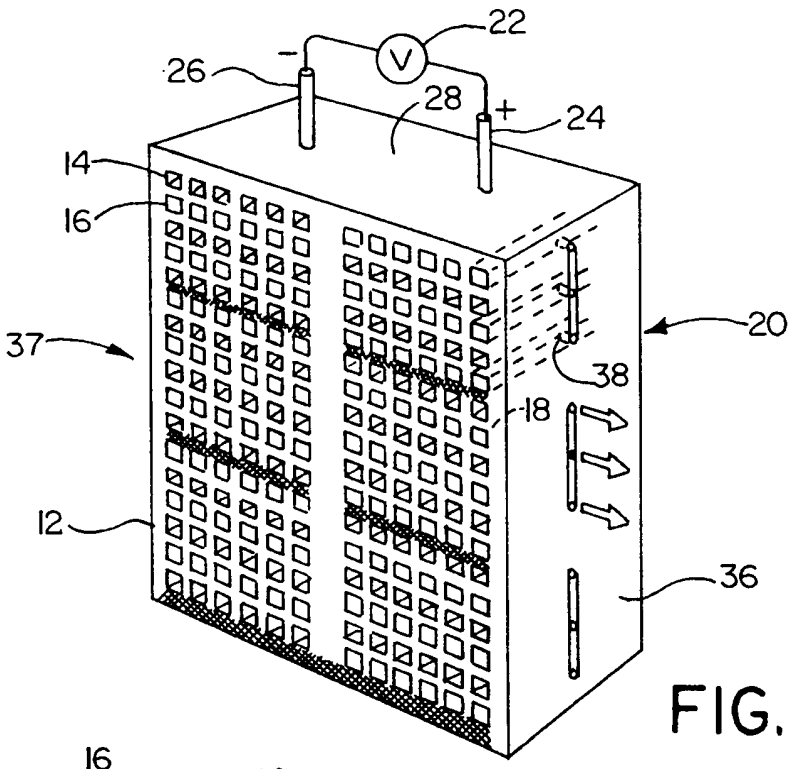


FIG. 1

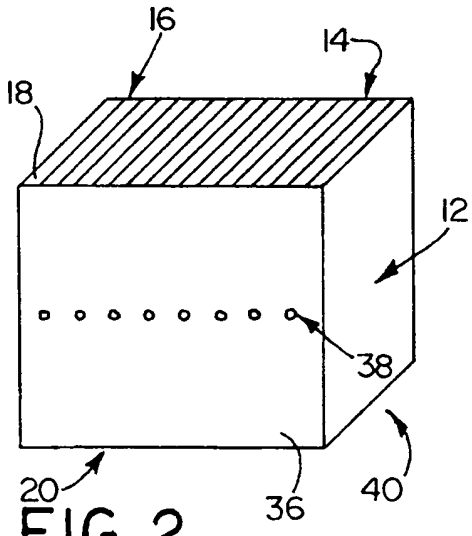


FIG. 2

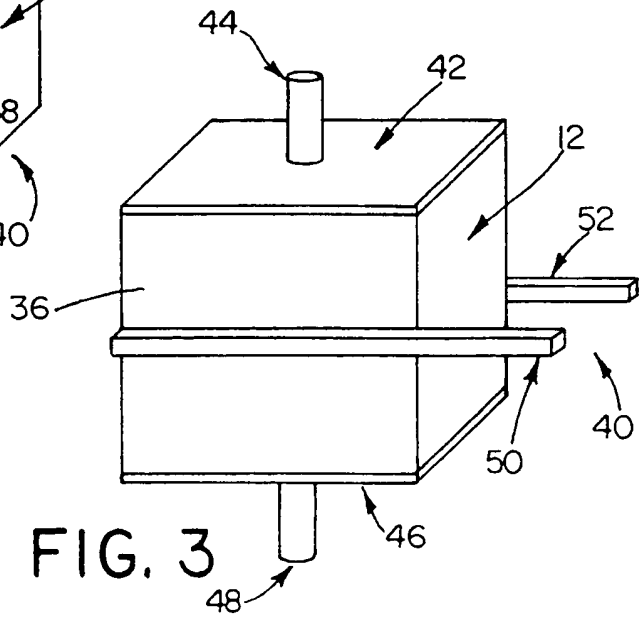


FIG. 3

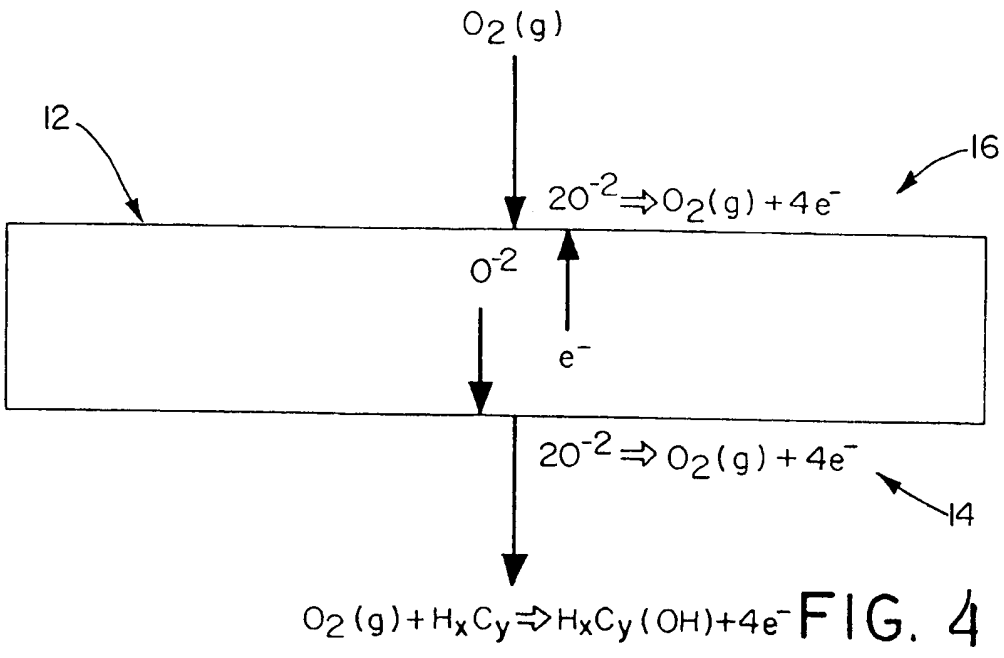


FIG. 4

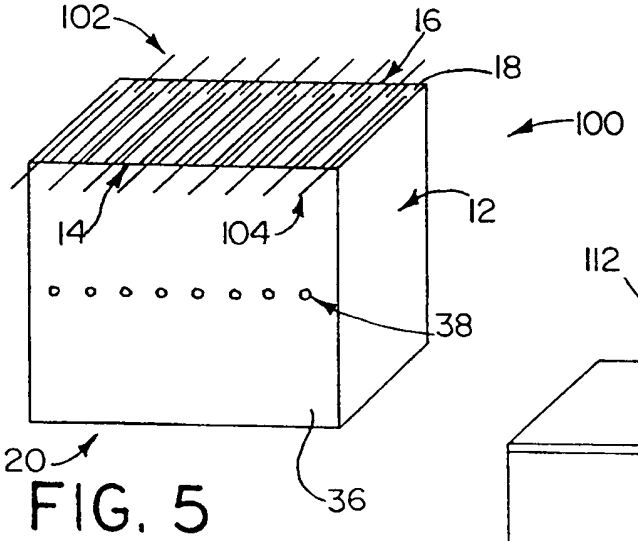


FIG. 5

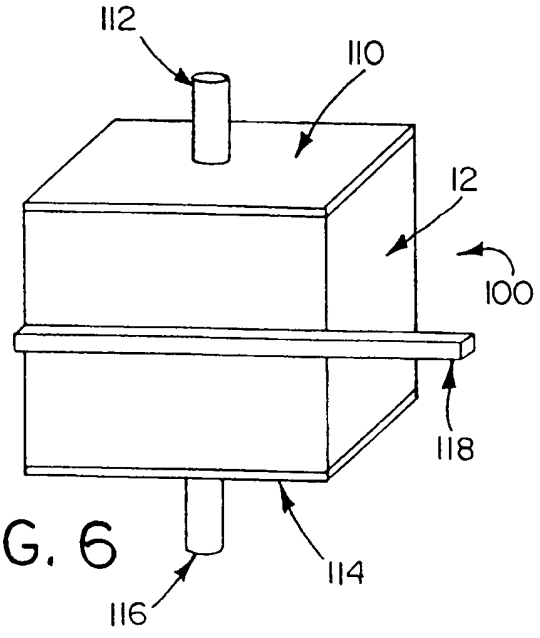


FIG. 6

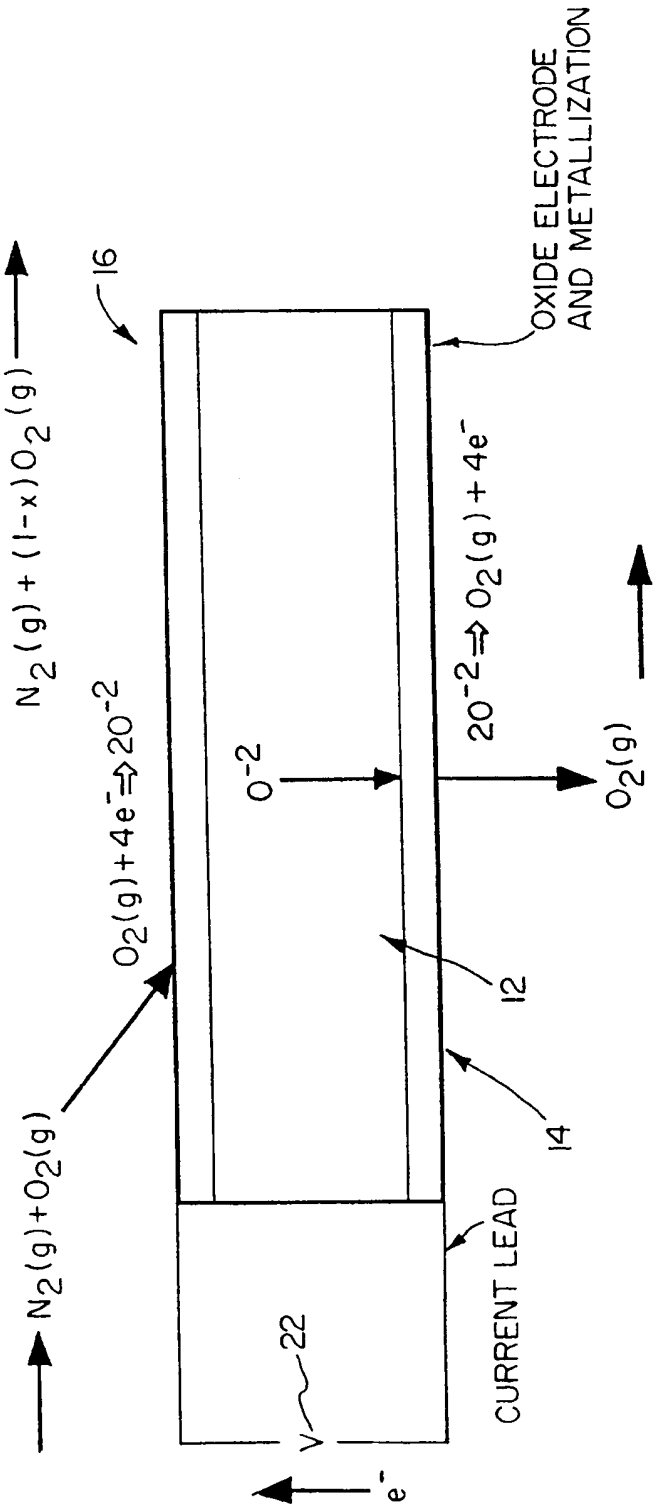

OXIDE ELECTRODE AND METALLIZATION
16
$N_2(g) + (1-x)O_2(g)$
$O_2(g)+4e^- \Rightarrow 2O^{-2}$
O^{-2}
$2O^{-2} \Rightarrow O_2(g) + 4e^-$
$O_2(g)$
12
14
$N_2(g)+O_2(g)$
CURRENT LEAD
22
V
e^-

FIG. 7

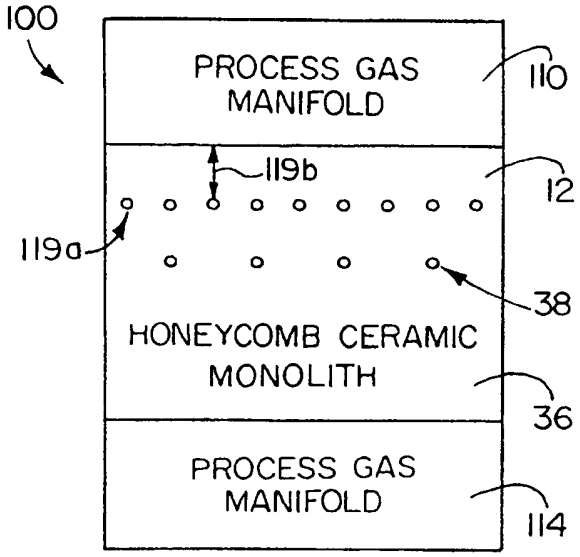


FIG. 7a

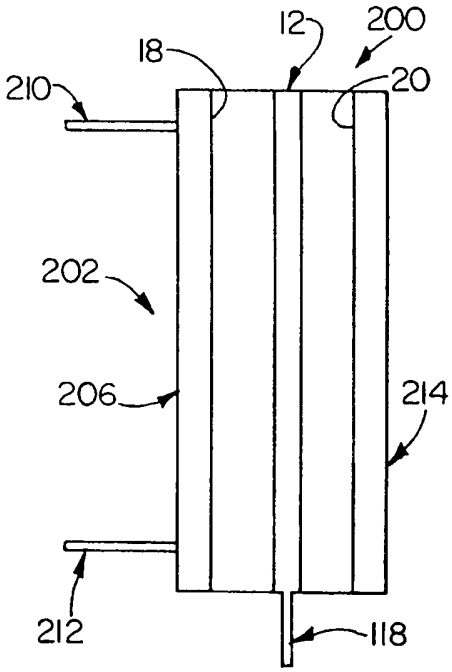


FIG. 8

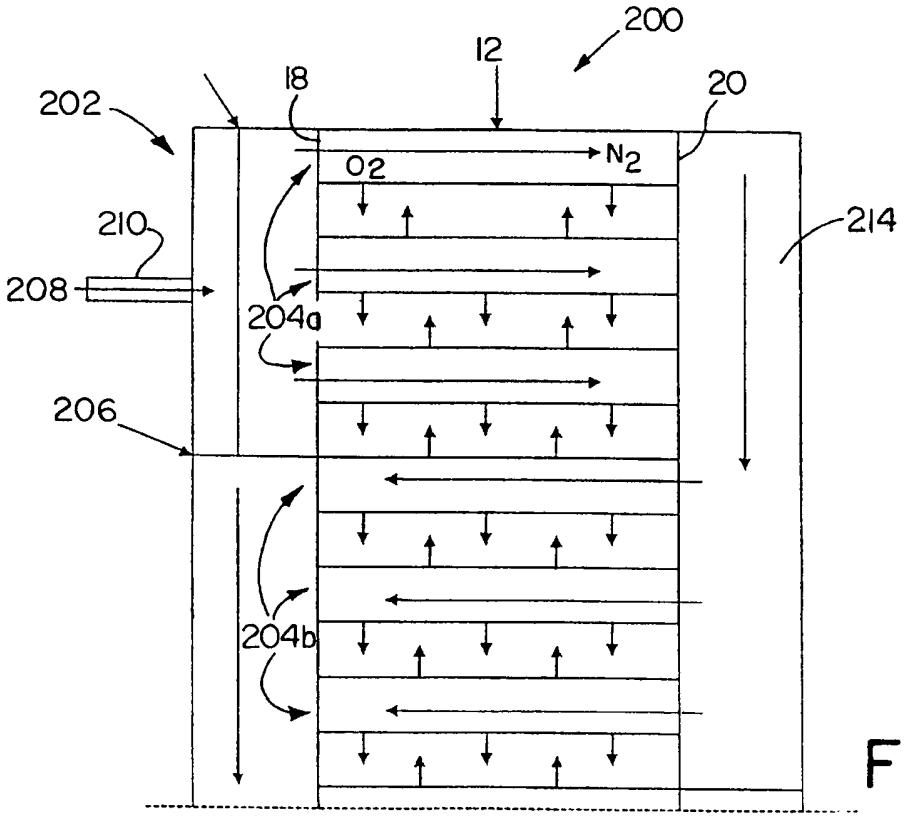


FIG. 9

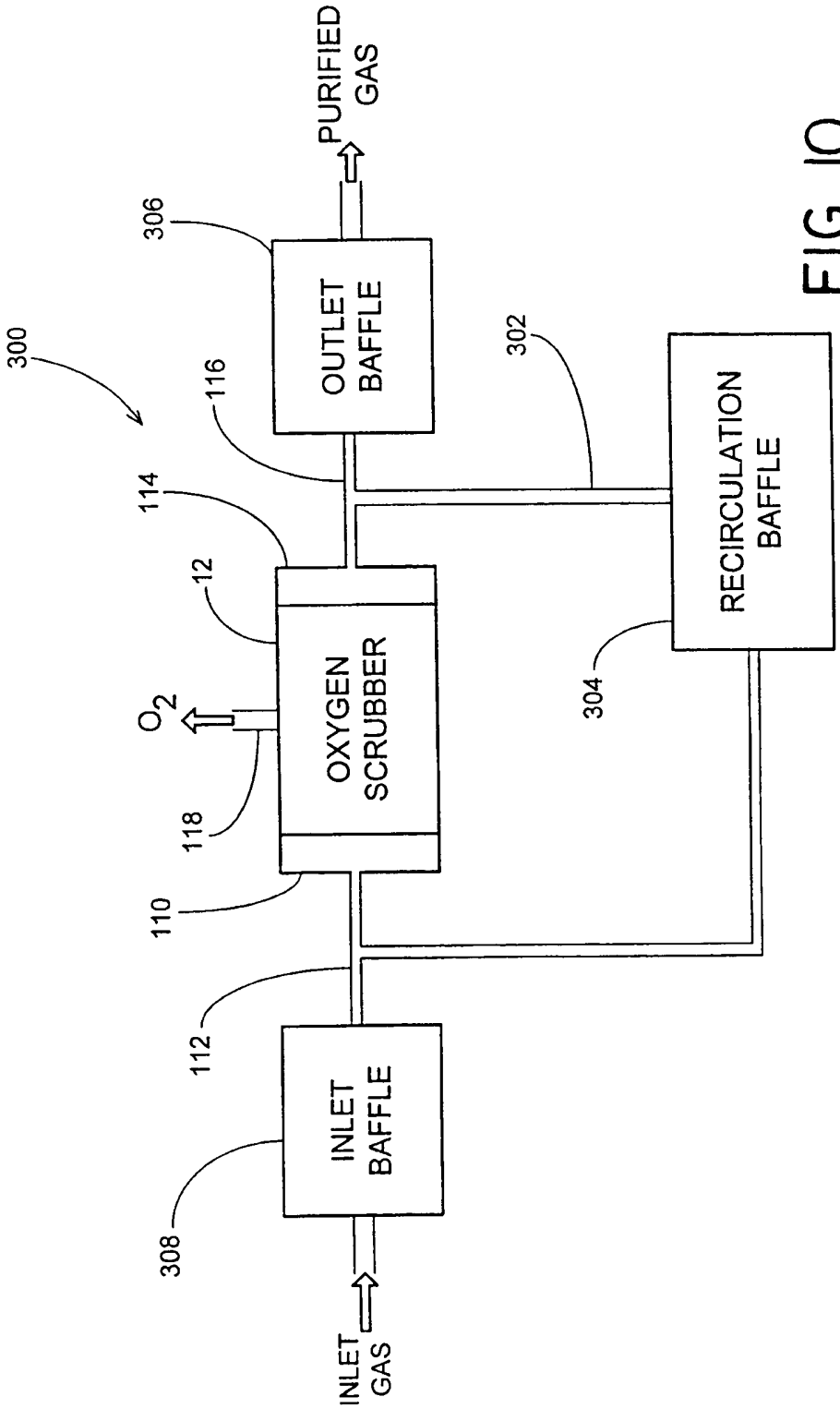
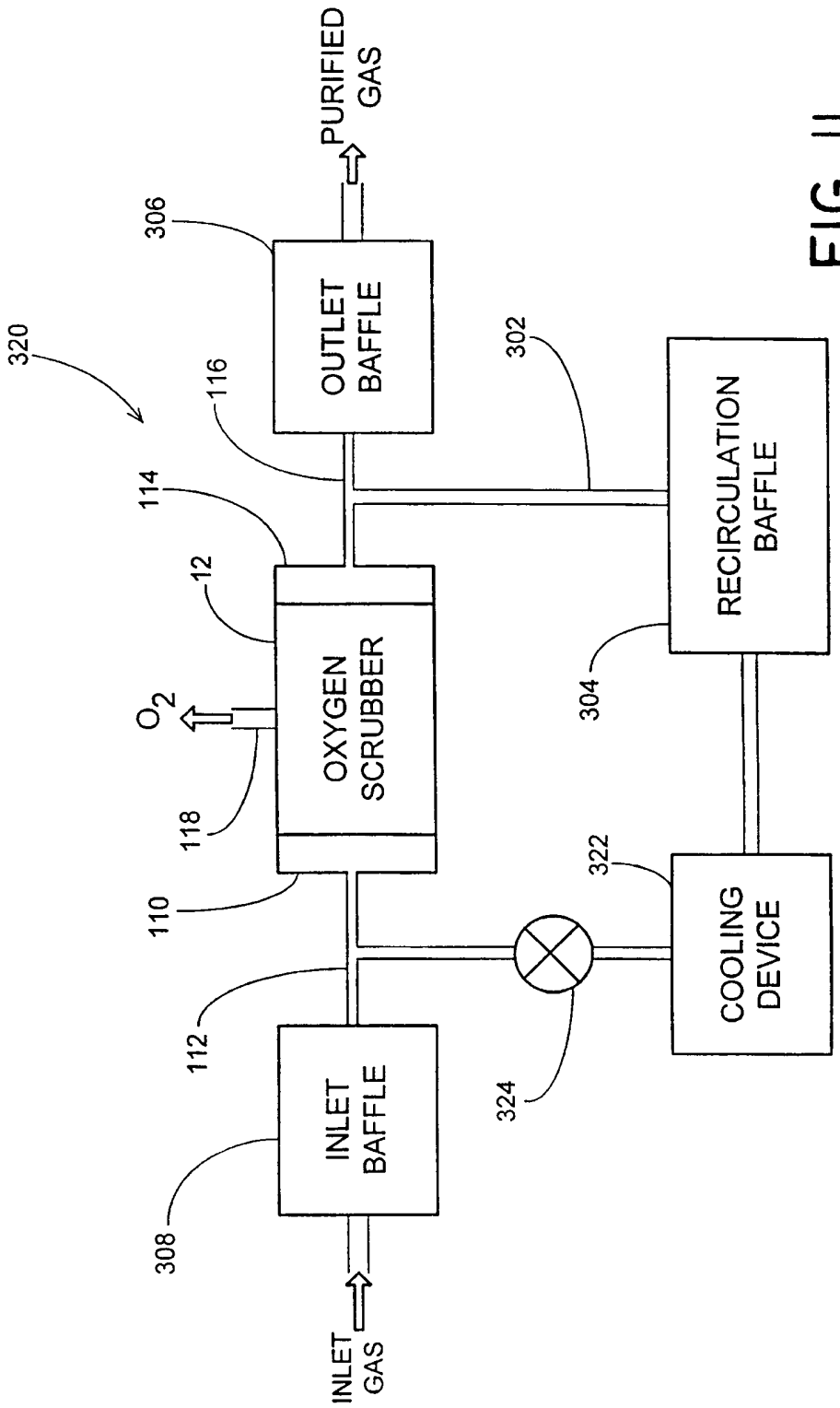

PURIFIED GAS
306
OUTLET BAFFLE
300
116
302
RECIRCULATION BAFFLE
114
12
OXYGEN SCRUBBER
O_2
304
118
110
112
INLET BAFFLE
308
INLET GAS

FIG. 10


PURIFIED GAS
306
OUTLET BAFFLE
320
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302
RECIRCULATION BAFFLE
114
12
OXYGEN SCRUBBER
O_2
304
118
322
110
COOLING DEVICE
112
324
INLET BAFFLE
308
INLET GAS

FIG. 11

INTERNATIONAL SEARCH REPORT

Interr ·al Application No
PCT/US 99/17404

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/32 C25B1/02 C25B9/00 H01M8/12 C01B13/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D C25B H01M C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 356 728 A (BALACHANDRAN UTHAMALINGAM ET AL) 18 October 1994 (1994-10-18) column 7, line 20 -column 8, line 54 column 15, line 28 -column 16, line 45 ---	1-18
Y	US 5 413 878 A (WILLIAMS MARK C ET AL) 9 May 1995 (1995-05-09) figures 1-10 ---	22-26
P,X	WO 99 29399 A (LAWLESS WILLIAM N ;CERAMPHYSICS INC (US)) 17 June 1999 (1999-06-17) page 8, line 10 -page 9, line 18; figures 1-5,7 --- -/--	11-21

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 November 1999	22/11/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Eijkenboom, A

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INTERNATIONAL SEARCH REPORT

Intern ial Application No
PCT/US 99/17404

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 205 990 A (LAWLESS WILLIAM N) 27 April 1993 (1993-04-27) cited in the application the whole document	11-21
Y		1-18, 22-26
X	US 3 950 944 A (MIURA YOSHINORI ET AL) 20 April 1976 (1976-04-20) the whole document	11,12, 15-21

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/US 99/17404

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